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(19)

(54) SOLID-LIQUID SEPARATION METHOD FOR ORGANIC WASTE SLUDGE

(71) We, TOKAI DENKA KOGYO KABUSHIKI KAISHA, a Japanese company, of Room 428 Ohtemachi Building, 6—1, 1—Chome, Ohtemachi, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to solid-liquid separation of organic materials in the treatment of aqueous sludges, e.g. from sewage, night soil and industrial wastewater.

Chemical, biological or other treatment has recently been applied for the treatment of sewage, night soil, or industrial wastewater. The biological treatments which produce lower biological oxygen demand (BOD) or chemical oxygen demand (COD) in effluent after the treatment has more recently found wider acceptance in view of wastewater control. In cases where chemical or physical treatment is carried out, conversion to or combination with biological treatment is adopted. In any of the above cited methods of treatment it is necessary to remove organic materials insoluble or suspended in water. For their rapid separation are used such reagents as lime, ferric chloride, ferrous sulfate and macromolecular flocculant.

A typical active sludge treatment method that is widely employed generally consists of an initial settling basin, an aeration tank, a final settling basin and a digestion tank for the effluent sludge. Separation of organic solid contents is needed during these steps for raw sludge from the initial settling basin, effluent sludge from the final settling basin and digested sludge from the digestion tank. Solid-liquid separation for these sludges has heretofore been performed with lime and ferric chloride and, recently in some instances, with macromolecular flocculant. These reagents, however, are not universally satisfactory for the solid-liquid separation of any sludge.

In a sewerage station receiving industrial waste-water, for instance, cake acceptable in solid-liquid separation for raw sludge is formed first by the addition of an excess of lime and ferric chloride; for the effluent sludge these reagents are not satisfactory for the best formation of flocs. As a matter of fact, the reagent is incorporated portion-wise into the raw sludge for the treatment. Consequently, the amount of lime and ferric chloride used is increased with the result that the amount of cake formed is also increased so that transportation and incineration of the cake as well as treatment of the ash after the incineration are very expensive. Furthermore, after the solid-liquid separation, the filtrate is alkaline with the lime and neutralizing it with sulfuric acid results in formation of gypsum, which clogs piping; expense for repair and maintenance of the piping cannot be neglected. Moreover, lime is undesirable from the work environment and hygiene-controlling point of view in that, being in the form of powder, it is liable to develop dust pollution and in some cases, contains much chromium, depending upon the origin. On the other hand, many of the macromolecular flocculants are toxic due to their molecular structures so that the solution after the solid-liquid separation will possibly be harmful to the organisms if returned to the active sludge.

According to one method, which is c ncerned with night soil treatment, hydrogen peroxide is effective in the solid-liquid separation even when mployed

alone and combined use of hydrogen peroxide with ferrous sulfate or ferrous sulfate and lime is also effective. Whereas application of hydrogen peroxide alone to solid-liquid separation of the organic sludge is feasible, the flocs formed are soft and friable and subsequent filtration and dehydration may be difficult depending upon such conditions as agitation, pH and temperature. With hydrogen peroxide and ferrous sulfate, ferrous ions flow out into the filtrate from the solid-liquid separation and may be harmful to the organisms if returned to the active-sludge-treatment step, although there are formed flocs hardly influenced by such conditions as agitation, pH and temperature, with the cake after filtration being acceptable.

In accordance with the present invention there is provided a method of solid-liquid separation in the treatment of organic waste aqueous sludge that comprises adding to the sludge from 0.5 to 30% by weight of hydrogen peroxide and from 0.1% to 10% by weight of a metal ion with at least trivalent positive charge on the basis of solid content of the sludge while maintaining the pH at or lower than 9 by the addition of an acid or alkali to form stable organic flocs and subsequently conducting solid-liquid separation by settling, suction or centrifugal separation process.

While this invention can overcome the disadvantages mentioned above, it provides a method of treatment that may offer many advantages over prior methods of treatment, e.g. with lime and ferric chloride, ferrous sulfate, or a macromolecular flocculant. Although the exact mechanism of the action of hydrogen peroxide and a metal ion with at least a trivalent charge is not understood, it is believed that the metal ions are electrically adsorbed upon the aggregates produced from organic insoluble or suspended materials with hydrogen peroxide by its aggregative action so that combined use of the two exerts such an effect entirely unexpected from the use of either of them. In fact, the flocs formed are so stable that they are by no means degraded under pH variation, temperature change and agitation and are filterable.

The method according to the invention will be described in embodiment below. For the raw sludge from the sedimentation sand basin in chemical or physical treatment, the settling basin in active sludge step or the initial storage tank in night soil treatment, the effluent sludge from the active sludge treatment step, or the digested sludge from the anaerobic treatment step, from 0.5% to 30% by weight of hydrogen peroxide in terms of pure substance on the basis of solid content of the sludge is employed. More particularly, the range is from 0.5% to 10% by weight for the raw sludge, from 4% to 20% by weight for the effluent sludge and from 0.5% to 30% by weight for the digested sludge, the last increased range being ascribed to concomitant removal of such products as hydrogen sulfide and mercaptans. It is economical to determine the proportion individually depending inter alia upon the nature of organic materials contained in the wastewater and reducible substances formed with the digested sludge after the anaerobic treatment. Hydrogen peroxide as defined in the present invention means not only hydrogen peroxide itself but also compounds that are soluble in water with evolution of hydrogen peroxide including sodium perborate, sodium percarbonate, calcium peroxide, persulfates and organic peroxides.

The metal ion with at least trivalent positive charge is added in a proportion in the range from 0.1 to 10% by weight on the basis of solid content of the sludge, more particularly from 0.1 to 5% with a raw sludge, from 1 to 7% with the effluent sludge and from 0.1 to 10% with the digested sludge. It is economically preferable to determine the proportion individually depending upon the product to be treated. As the metal ion with 3 or higher valency may be mentioned Fe^{3+}, Al^{3+}, Cr^{3+}, Cr^{6+}, Ti^{4+}, V^{3+}, V^{4+} and V^{5+}. Cr^{3+}, being toxic, and Ti and V compound being expensive are undesirable. In general, Fe^{3+} and Al^{3+} are preferred.

Selection of the acid or alkali used for maintaining the pH at or lower than 9 is dependent upon the liquid properties of the sludge. Preferably, mineral acids such as hydrochloric, sulfuric and phosphoric acids and organic acids are used as the acid and salts with inorganic acids such as sodium hydroxide, sodium carbonate and calcium carbonate. Since the active sludge is usually under nearly neutral conditions in liquid phase, use of a conventional metal salt such as, for example, ferric chloride, aluminum chloride, ferric sulfate or aluminum sulfate would allow an acid to remain following adsorption of the metal ion on the floc with the result that the pH would be maintained at or lower than 9. A pH above 4 is preferred because of development of corrosion in the equipment at pHs at or below 4.

Advantages of the present invention can have over the prior method with lime and ferric chloride are enumerated below:

(i) Enhancement of the solid-liquid separation and remarkable improvement of the degree of dehydration after passage through the filter cloth. Whereas the rate of filtration is 4 $kg/m^2/H$ with the prior-art method for the raw sludge, it is increased to 6 $kg/m^2/H$ with the method of the invention.

(ii) Feasibility of the treatment with a higher solid content in the sludge. Whereas the solid content has to be 2% or lower with large pressure filtration equipment according to the prior art method, it is feasible to increase it to 5% according to the method of the invention.

(iii) Marked decrease in water content of the filter cake. Whereas it is 50—55% with the prior art method, it is 40—50% with the method of the invention.

(iv) Decrease in amount of the cake proportional to the amount of lime, being from 1/2 to 3/4 the amount with the prior art method depending upon the amount of lime added.

(v) Advantage in incineration of the cake. Whereas inner temperature of the furnace was 600—700°C with the prior art method even if incinerated with heavy oil, it was raised to 800—900°C with amount of the heavy oil decreased with the method of the invention. Amount of the ash after the incineration was also decreased to less than 1/2 as compared with the prior method.

(vi) High deodorant activity with improvement of the work environment. Hydrogen peroxide is reacted with hydrogen sulfide and mercaptans to deodorize substances so that the work room becomes almost odorless.

(vii) No need of neutralization of the filtrate. It is necessary to conduct the neutralization with sulfuric acid with the prior art method in which a filtrate with a pH from 10 to 11 is removed. According to the method of the invention, the pH is in the range between 5 and 8, thus avoiding the need of neutralization with the result that clogging of the piping by gypsum formed after the neutralization does not take place.

(viii) No problem of lime pollution. Whereas problems occur with lime which is in powder form of dust pollution and, in some instances depending upon origin of the lime, incorporation of chromium, there is no need in the method of the invention of considering these problems.

(ix) Ease of introducing workerless operation into the equipment. It is necessary in the prior art method to bring lime in the form of powder to the equipment in which it is dissolved in water. The procedure is unnecessary in the method of the invention, into which workerless operation is easily introduced.

(x) Lower cost.

The invention will be described in greater detail in conjunction with the following specific examples. They are submitted to illustrate the invention. The proportions in the specification, examples and claims are by weight unless otherwise indicated.

Method:

Samples of sludge were admixed with a predetermined amount of hydrogen peroxide and a metal ion and then, pH being adjusted to 9 or below, subjected in either of the laboratory equipments described below to filtration and dehydration.

(1) Small pressure filtration equipment.

Five liters of a reagent-treated sludge were placed in a closed storage vessel, into which was introduced nitrogen gas under predetermined conditions of pressure and time for filtration. The sludge was passed under pressure to a prearranged closed filtration vessel, in which the solid content remained on the filter cloth and the filtrate was discharged. The introduction of nitrogen gas under pressure into the storage vessel was then terminated and nitrogen gas was introduced under pressure directly into the filtration vessel. The solid content on the filter cloth was dehydrated under the pressure for the period of time for the compression. Cake thus formed was measured for weight, thickness, peeling from the cloth and water content.

(2) Large pressure filtration equipment (Ukraina Filter manufactured by Tsukishima Kikai).

Three cubic meters of a reagent-treated sludge was introduced under pump pressure for a predetermined period of time into the filter. Then, air was introduced by means of a compressor under a predetermined condition of compression for dehydration. Cake thus formed was measured in the same way as under (1) above.

Comparative Example 1:

To a raw sludge with a solid content of 2—3% were added 30—50% by weight of lime [$Ca(OH)_2$] on the basis of the solid content and 10—13% by weight of ferric chloride ($FeCl_3$) on the basis of the solid content. The mixture was treated in small and large filtration equipment. Filtration was done under a pressure of 3 kg/cm² for 6 min. and the compression at 10 kg/cm² for 10 min. A number of samples were tested and the data are set forth in Table I (numbers 1—7).

TABLE I

No.	Equipment	Solid Content (%)	On the solid content (%)			pH of the Appearance	cake				Filtration Rate (kg/m²/H)
			$Ca(OH)_2$	$FeCl_3$	Filtrate		Peeling	Thickness (mm)	Water Content (%)		
1	Small	3	30	6	10.0	Bad	Bad	—	67		—
2	,,	,,	40	7	10.5	Good	Good	2.5	56		3.8
3	,,	,,	50	9	11.0	,,	,,	3.1	53		4.2
4	Large	2	40	7	10.5	Poor	Bad	3.2	61		3.1
5	,,	,,	45	8	11.0	Good	Good	2.6	54		4.1
6	,,	,,	50	9	11.2	,,	,,	2.9	57		4.5
7	,,	,,	,,	9	11.0	Bad	Bad	—	—		—

EXAMPLE 1.

To a raw sludge with a solid content of 2—5% were added 1%—3% by weight of hydrogen peroxide (H_2O_2) in terms of the pure substance on the basis of the solid content and 3%—6% by weight of ferric chloride on the basis of the solid content. The mixture was thoroughly admixed and treated in small and large filtration equipment. Filtration was done under a pressure of 3 kg/cm² for 6 min. and the compression at 10 kg/cm² for 10 min. A number of examples of the invention were run and the data are set forth in Table II (numbers 8—17).

TABLE II

			On the solid content (%)				cake			
No.	Equipment	Solid Content (%)	H_2O_2	$FeCl_3$	pH of the Filtrate	Appearance	Peeling	Thickness (mm)	Water Content (%)	Filtration Rate (kg/m²/H)
8	Small	2	2.5	4	5.0	Good	Good	2.8	42	6.0
9	,,	3	,,	,,	5.2	,,	,,	3.3	44	5.7
10	,,	4.2	,,	,,	5.5	,,	,,	4.2	48	5.2
11	,,	5	,,	,,	,,	,,	,,	5.0	50	4.8
12	,,	3	1	3	5.6	,,	,,	4.6	52	4.2
13	,,	,,	2	4	5.1	,,	,,	4.4	45	5.4
14	,,	,,	3	6	4.8	,,	,,	5.1	40	6.3
15	Large	2	2.8	5	6.5	,,	,,	4.0	42	5.2
16	,,	2.8	,,	,,	,,	,,	,,	3.3	46	4.6
17	,,	3.6	,,	,,	7.2	,,	,,	4.5	50	4.4

EXAMPLE 2.

Comparison was made between the method involving use of lime and ferric chloride and that of hydrogen peroxide and ferric chloride for an effluent sludge containing 0.8% solid. The filtration was done under a pressure of 3 kg/cm^2 for 10 min. and the compression at 10 kg/cm^2 for 15 min. These data are in Table III (numbers 18—22).

TABLE III

No.	Equipment	Solid Content (%)	On the solid content (%)			cake			Filtration	
			$Ca(OH)_2$	H_2O_2	$FeCl_3$	Appearance	Peeling	Thickness (mm)	Water Content (%)	Rate ($kg/m^2/H$)
18	Small	0.8	100	—	10	Bad	Bad	—	—	—
19	,,	,,	150	—	15	,,	,,	—	—	—
20	,,	,,	—	6	5	Good	Good	2.7	68	2.9
21	,,	,,	—	7	6	,,	,,	3.3	58	3.4
22	,,	,,	—	9	7	,,	,,	3.5	53	4.1

EXAMPLE 3.

Comparison was made between the method involving use of lime and ferric chloride and that of hydrogen peroxide and aluminum sulfate [$Al_2(SO_4)_3$] for a digested sludge containing 2% solid. These data are in Table IV (numbers 23—27).

TABLE IV

No.	Equipment	Solid Content (%)	On the solid content (%)				cake		Filtration		
			$Ca(OH)_2$	H_2O_2	$FeCl_3$	$Al_2(SO_4)_3$	Appearance	Peeling	Thickness (mm)	Water Content (%)	Rate ($kg/m^2/H$)
23	Small	2	30	–	6	–	Poor	Poor	4.0	67	2.5
24	,,	,,	50	–	9	–	Good	Good	3.5	55	3.8
25	,,	,,	–	1	–	6	,,	,,	4.3	57	3.1
26	,,	,,	–	2	–	8	,,	,,	2.9	51	4.3
27	,,	,,	–	3	–	12	,,	,,	3.0	49	4.2

WHAT WE CLAIM IS:—

1. A method of solid-liquid separation in the treatment of organic waste aqueous sludge that comprises adding to the sludge from 0.5 to 30% by weight of hydrogen peroxide and from 0.1% to 10% by weight of a metal ion with at least trivalent positive charge on the basis of solid content of the sludge while maintaining the pH at or lower than 9 by the addition of an acid or alkali to form stable organic flocs and subsequently conducting solid-liquid separation by settling, suction or centrifugal separation process.

2. A method as claimed in Claim 1 in which the sludge is raw sludge and 0.5% to 10% hydrogen peroxide with 0.1% to 5% metal ion with at least trivalent positive charge is used.

3. A method as claimed in Claim 1 in which the sludge is effluent sludge and 4% to 20% hydrogen peroxide is utilized with 1% to 7% metal ion having at least trivalent positive charge.

4. A method as claimed in Claim 1 in which the sludge is digested sludge.

5. A method as claimed in any preceding claim in which the metal ion is Fe^{3+} or Al^{3+}.

6. A method as claimed in any preceding claim in which the pH is maintained above 4.

7. A method as claimed in Claim 1 substantially as hereinbefore described in any one of the foregoing Examples.

8. Organic waste sludge produced by a method as claimed in any one of Claims 1 to 7.

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